ENANTIOMERIC DERIVATIZATION ON THE MARS ORGANIC MOLECULE ANALAZER (MOMA) EXPERIMENT ABOARD EXOMARS 2018: HOW TO UNRAVEL MARTIAN CHIRALITY. C. Freissinet[1,2], A. Buch[3], C. Szopa[4], V. T. Pinnick[1], M. Morisson[3], N. Grand[5], F. Raulin[5], W. B. Brinckerhoff[1]. [1]NASA Goddard Space Flight Center, Greenbelt, MD, caroline.freissinet@nasa.gov, [2]NASA Postdoctoral Program, Oak Ridge Associated Universities, TN, [3]Ecole Centrale Paris, Chatenay-Malabry, France, [4]LATMOS-UVSQ-UPMC, Paris, France. [5]LISA-UPEC, Creteil, France.

Introduction: The origin of homochirality in life on Earth remains unknown. The answer to this question lies in the study of chirality elsewhere in the Solar System. The Sample Analysis at Mars (SAM) experiment aboard Curiosity established the presence of organic molecules indigenous to a clay-rich sample on Mars [1]. However, SAM does not have the ability to separate between the enantiomers of potential medium- or high- molecular weight organic molecules. One of the wet chemistry experiments to be used in the MOMA instrument of the Exomars mission is designed for the extraction and identification of refractory organic chemical components in solid samples using gas chromatography-mass spectrometry (GCMS), while keeping the chiral center of the molecules intact [2]. This derivatization technique, using dimethylformamide dimethylacetal (DMF-DMA) as a reagent, will allow MOMA to separate the enantiomers of molecules of interest for astrobiology, such as amino acids, sugars or carboxylic acids. We present here the results of laboratory experiments which display the feasability and limitations of the detection of an enantiomeric excess of complex organic molecules in various analog samples, depending on the mineralogy of the Mars analog solid sample.

Discussion: DMF-DMA can react with a broad range of molecules containing a labile hydrogen such as alcohols, primary and secondary amines, carboxylic acids and amino acids in the free form. The methylated products of these molecules are typically much more volatile than the original non-derivatized molecule, which enables the transfer of the DMF-DMA derivatives for GCMS analysis. Moreover, derivatization with DMF-DMA keeps the chiral center of the molecules intact, which allows for an enantiomeric separation on a chiral GC column downstream (Figure 1).

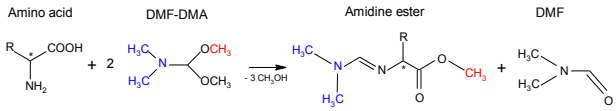

Fig. 1: example of DMF-DMA derivatization on a chiral amino-acid. The derivatization preserves the chiral center of the molecule. Both derivatives' enantiomers can further be separated on a chiral GC column.

Racemisation (interconversion between L- and R-enantiomers) of chiral compounds can occur, especially when the molecules are heated or reside in wet conditions. The conditions of analysis during a derivatization experiment can thus interfere with the pristine enantiomeric state of the molecules present in the sample. Laboratory experiments on various analogs are thus necessary to establish the influence of the mineralogy in the racemization process of the organic molecules, under the conditions used for MOMA DMF-DMA derivatization. As an example, the water released from clay minerals may enhance the racemization, while organics preserved in sulfate samples would be more resistant to racemization. The laboratory studies are essential to pin down windows of preservation of organic molecules, and preservation of their enantiomeric state.

Moreover, MOMA will perform a new one-pot/one-step extraction and derivatization of the molecules from the solid sample. Because of the additional constraints imposed by such a process, a similar experiment using the MOMA capsules containing the derivatizating reagent was performed in the laboratory, using a range of analog samples representing mineralogies likely to be encountered at Mars. The interactions between the molecules and the minerals is strongly dependant on the mineralogy of the sample, as is their extraction. The preliminary results show that even if more optimization is needed to have an optimal yield of recovery of organic molecules from the sample, we were able to detect a range of organics structures and also to separate and quantify their enantiomers in MOMA-like laboratory analyses.

References: [1] Freissinet *et al.* (2015) *JGR Planets, accepted.* [2] Freissinet *et al.* (2011) *J. Chrom. A* , 1217, 731-740.